

## SOME PROBLEMS IN THE MODELING OF COMPLEX CHEMICAL PROCESSES

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### INTRODUCTION

In the last decade, the "mature" science of chemical kinetics has entered what may be termed the "Computer Age". Thirty years ago, the goal of chemical engineers working with a chemical process would be to obtain an explicit rate expression describing the rate dependence on experimental parameters. For diverse reasons, this is no longer a sufficient result. The availability of high speed computers together with relevant kinetic and thermochemical data have today made possible the description of a complex chemical process in terms of the elementary kinetic steps comprising it. Explicitness is no longer necessary

This evolution has been accelerated by a need to satisfy increasingly stringent environmental requirements as well as the need to reduce the cost of optimization of chemical processes. Experiments, particularly in larger scale equipment can become prohibitively expensive and time consuming. Computer experiments, on the contrary are inexpensive and can be adapted, in combination with the appropriate fluid mechanics, to rapid and inexpensive scaling. Laboratory experiments in 1 cm diameter tubing are relatively cheap and easy to do but may not represent the results of an industrial flow process carried out in 10 cm to 20 cm pipes.

Fuel chemistry has been one of the pioneers in adapting computer kinetics to its various needs. In doing so it has brought together the chemical engineer, the academic kineticist and the fluid dynamicist in what is truly today, a multi-disciplinary effort. Despite the considerable reluctance of each of these specialists to interact with each other, there is no alternative to a directed and active dialogue. This "social" barrier has been little discussed but has been as much a challenge as the technical problems themselves. From my own experience as an academic kineticist who has done much industrial consulting, I would estimate that the usual mode of arms length interaction between kineticist and engineers has generated a 10 to 20 year lag in the utilization of basic science. A good part of this lag arises from difficulties in the basic kinetic science itself and this is the subject I would like to discuss here.

Kinetic modeling of a complex chemical process requires the following:

- 1.) A complete knowledge of the elementary kinetic steps--the mechanism.
- 2.) Accurate thermochemical data on all of the species involved.
- 3.) Accurate kinetic data for each step.
- 4.) An understanding of surface processes which may be of importance.

Historically, the first attempt to model a complex system was the Rice-Herzfeld analysis of the thermal cracking of hydrocarbons almost 60 years ago.<sup>1</sup> While enormously simplified compared to our current understanding this work provided the prototype for all subsequent efforts. The problems, then as now remain the same, namely, the four requirements outlined above.

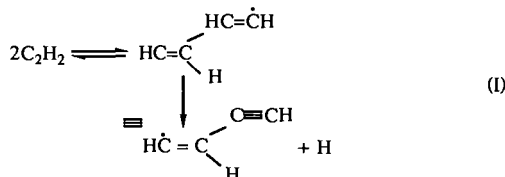
### Mechanism

It is impossible to prove that any given mechanism is correct or complete. Its operational test is that it reproduces quantitatively all available data on any chemical process. An interesting example is provided by the pyrolysis of acetylene. While early work on acetylene had been interpreted in terms of a free radical mechanism<sup>2</sup> recent workers have tried to interpret this chemistry in terms of an active carbene isomer of acetylene, vinylidene:<sup>3,4</sup>

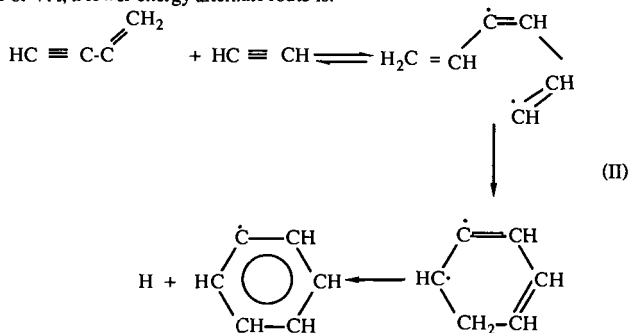


The reason for invoking such a species was that the conventional free radical mechanism could not account for the observed rate of pyrolysis of acetylene by as much as a factor of 100 at 1000°K. However, a recently proposed mechanism invoking a different radical initiation process has been shown to account for all the features of  $\text{C}_2\text{H}_2$  pyrolysis.<sup>5</sup>

This most recent free radical mechanism makes use of vinyl acetylene (VA), the first product of acetylene pyrolysis, as an autocatalytic agent which provides a fast low energy path to free radical initiation. In the absence of VA free radicals are provided by a bimolecular process:



In the presence of VA, a lower energy alternate route is:



This second path (II) has an activation energy of 30 kcal whereas the first path (I) has  $E = 67$  kcal. Using estimated rate constants consistent with the data on VA-acetylene copyrolysis<sup>6</sup> it turns out that at a  $[\text{VA}]/[\text{C}_2\text{H}_2]$  ratio of  $10^{-7}$  at 800°K the two paths are equal in rate. The well documented induction period in acetylene pyrolysis is then the time required via slow initiation path (I) to produce the small amounts of VA needed to permit path (II) to take over as the initiation source.



### Surface Processes

Surface chemistry still represents the very gray area of modeling. We have very little detailed knowledge of the thermochemistry or kinetics of surface reactions. Anyone who has worked with high temperature pyrolysis reactions is familiar with "coking" in hydrocarbon systems and the importance of surface generated reactions. In the past two years the discovery of important reactions on the surfaces of nitric acid ice crystals in the Antarctic stratosphere has provided an unexpected jolt to the atmospheric kineticists. Recent work on diamond formation from  $\text{CH}_4$  at high temperature has given an enormous stimulus to the study and understanding of radical reactions of surfaces.<sup>10</sup> Hopefully, this will produce some quantitative kinetic and thermochemical data from which we can build a systematic base. For the moment, surface reactions will continue to be treated empirically.

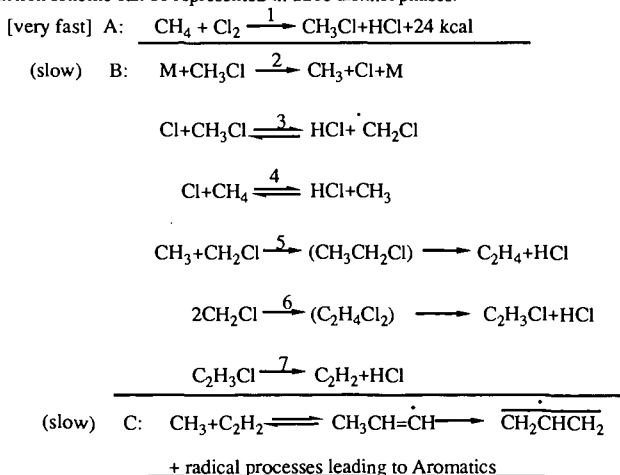
It is well however to note that for radical-molecule reactions at surfaces, these are essentially members of the gas phase family subject only to non-bonded interactions due to steric crowding.

Metals and metal oxides may differ basically from hydrocarbon surfaces in that they present very polar environments and their reactions may resemble ionic or ion-pair reactions rather than the mildly polar reactions of hydrocarbons and their radicals.

Equally of note is the fact that there is a large loss in entropy for a gas phase species on chemisorbing at a surface site. We can estimate entropies of chemisorbed species to an accuracy of about 1-2 cal/mole $^\circ\text{K}$  so that with a knowledge of the surface concentration we can estimate heats of chemisorption to 1 kcal.

### The High Temperature Reaction of $\text{Cl}_2 + \text{CH}_4$

A recent example of modeling with importance in C-I chemistry has just been done in my laboratories at USC.<sup>11</sup> We have modeled the reactions of  $\text{Cl}_2 + \text{CH}_4$  mixed hot at 700 to 900 $^\circ\text{K}$ . It is an extremely rapid, exothermic reaction capable of reaching peak temperatures of 1400-1500 $^\circ\text{K}$ . The reaction scheme can be represented in three distinct phases:



Modeling has shown that the gas phase reaction will produce up to 70 and 80% of useful products per mole  $\text{Cl}_2$  with about 78% conversion of  $\text{CH}_4$  per pass. Useful products are predominantly  $\text{C}_2\text{H}_2 + \text{C}_6\text{H}_6$  with lesser amounts of ethylene, butadiene, vinyl chloride, and styrene. Only trace amounts of naphthalene or higher species are formed.

Comparison with laboratory data in high surface reactors suggest that only surface reactions can account for the carbon formation observed at longer residence times. This system which represents an economically attractive methane convertor presents some very interesting engineering problems; rapid mixing of hypergolic species, hot  $\text{Cl}_2 + \text{CH}_4$  and rapid quenching (100 msec) of the reaction stream before significant surface reactions have occurred.

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## KINETIC STABILITY OF UNSATURATED ORGANICS AT HIGH TEMPERATURES

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### Introduction

Key words: unsaturated organics, kinetics, decomposition

Chemical processes involving organic compounds at high temperatures are controlled largely by the chemical and thermal stability of the unsaturated compounds that are formed during the decomposition process. This report reviews recent quantitative work dealing with these questions in the context of the thermal kinetics of reactions of such molecules in purely pyrolytic systems. It will also seek to highlight some of the important uncertainties in the understanding of the kinetics of such systems. The paper will begin with a summary of the present state of knowledge on the strength of the bonds (bond dissociation energies) that hold an unsaturated compound together. This will be followed by discussions on unimolecular reactions of molecules and radicals. For the former, bond dissociation and molecular processes will be considered. In the case of radicals, interest is on dissociation and isomerization. Bimolecular processes to be covered include metathesis and radical addition to stable compounds and radical combination with other radicals. Many of these processes are relatable to each other through the equilibrium constants. Thus the correct thermochemistry for reaction intermediates will be an underlying theme throughout this paper.

### Bond Energies

The addition of unsaturation to an alkane leads to drastic changes in the strength of the bonds in the molecule. The general situation in terms of a number of typical cases is summarized in Figure 1<sup>1-4</sup>. It can be seen that the bonds immediately adjacent to the site of unsaturation are strengthened, while those beta to that site are weakened. Thus the smallest unsaturates such as ethylene and acetylene, in terms of bond breaking through unimolecular decomposition, are rendered more stable. Indeed, for these compounds, unimolecular bond cleavage is probably not an important initiation reaction in comparison to radical induced decomposition processes under the conditions of most practical systems. For larger species, unsaturation leads to destabilization. This is a direct manifestation of the resonance energy of the new radicals that are formed.

There are still considerable uncertainties on the exact values of the bond energies given above. This may not be too serious for many high temperature applications, since the dependence on the activation energies decrease with temperature. It is however less satisfactory in cases where accurate branching ratios are required. As will be surmised from the subsequent discussion, there is now good capability for extrapolation and interpolation. Predictions can still be subject to large errors.

### Unimolecular Decomposition Processes

Table 1 contains rate expressions for bond breaking processes involving olefins<sup>2</sup>, aromatics<sup>4</sup>, alkynes<sup>2</sup> and a representative alkane<sup>2</sup>. All the reactions of the unsaturated compounds lead to the formation of resonance stabilized radicals and represent important dissociation channels. It can be seen that the differences in the activation energy from the alkane can be accounted quite accurately by the resonance energy. There is also a consistent decrease in the A-factor for the decomposition of the unsaturated compounds. It is possible to account for this by the more "tightened" structure of the resonance stabilized radical in comparison to that of the alkyl radicals formed during the decomposition of the alkanes. Of particular interest are the three dienes, 1,7-octadiene<sup>5</sup>, 1-7 octadiyne<sup>7</sup> and 1,5 hexadiene<sup>8,6</sup>. In the first case, the results are consistent with the assumption that substitution gamma to the bond being broken will have negligible effects. There is a factor of 2 divergence from this correlation for 1,6octdiyne. The data for 1,5 hexadiene are derived from the results on the allyl combination process. Although the A-factor appears to be slightly smaller than what would have been expected on the basis of the general trends, the discrepancies are not particularly large. Thus given the rate expression for an alkane it is quite straightforward to derive a similar expression for an unsaturated compound.

The resulting rate expressions leads to rate constants that are consistently larger than that for the comparable alkanes. This is especially true at the lower temperatures where the activation energies have larger effects on the rate constants. Unlike the alkanes, the larger unsaturated compounds can also decompose through a molecular "retro-ene" channel. This involves passage through a six centered transition state<sup>2</sup>. Some experimentally determined rate expressions can be found in Table 3.<sup>1</sup> Figure 2 contains Arrhenius plots for decomposition of 1-hexene and 1-hexyne through bond breaking and retro-ene channels. The larger rate constants for C-C bond cleavage in 1-hexene compared to that for 1-hexyne are entirely due to the change in the resonance energy of the two radicals formed during decomposition. However, the ordering is reversed for the molecular decomposition channel. From purely geometric considerations one would have thought that the preference would have been for 1-hexene since the 120° C=C-C bond angle in this compound should have resulted in less strain in the transition state than the linear C-C-C structure in 1-hexyne. The consequence is that the molecular process is more likely to be important for the decomposition of the latter. Interestingly, for the alkylbenzenes the retro-ene process appears to be much less important. At 1100 K it has not been possible to detect any contribution from this source in the decomposition of n-pentylbenzene<sup>4</sup>. In general, molecular channels becomes increasingly important with greater unsaturation. Thus, the predominant modes of 1,5 hexadiyne decomposition is to benzene and fulvene<sup>8,9</sup>.

Where there are no C-C bonds for which cleavage leads to resonance stabilized radicals, then the weakest bonds are the resonance destabilized C-H bonds. This however only moves these values to the upper end of the numbers for C-C bond cleavage in alkanes. Furthermore, the A-factor for C-H bond break can be expected to be somewhat smaller than that for C-C bond cleavage. An interesting situation arises for compounds such as propene and toluene where there the breaking of the C-C bond next to the site of

unsaturation may become competitive with that for C-H bond cleavage. In the case of toluene the experimental data are controversial<sup>10-11</sup>. The situation is made more uncertain by the fact that at the high temperatures required for these decompositions, the reactions are into the pressure dependent region. Thus it is not only necessary to have accurate high pressure rate expressions but also the energy exchange parameter. A satisfactory fit of the data pertaining to propene decomposition have been published recently<sup>12</sup>.

The stability of the small unsaturated compounds also brings into play the possibility of other modes of decomposition. Thus in the case of ethylene<sup>13</sup>, there is considerable evidence for a reaction channel involving vinylidene. For butadiene decomposition the data is suggestive of an analogous process<sup>14</sup>. In the case of cis-butene-2 the decomposition data have been interpreted in terms of the direct formation of butadiene<sup>15</sup>. In the case of benzene however, C-H bond cleavage appears to be the predominant decomposition mode under all conditions<sup>16</sup>. Another initiation process that is unique to unsaturated compounds is the possibility of radical formation through bimolecular reaction or the reverse of radical disproportionation reactions<sup>17</sup>. Rate expressions for these processes can be readily derived through the equilibrium constant and well established rate constants for the latter on the assumption that the temperature dependence of the disproportionation process is small.

There are very little data on the kinetics of the decomposition of unsaturated radicals. For the vinyl radical, one can calculate a high pressure rate expression on the basis of the reverse reaction and the thermodynamics<sup>13</sup>. However, under practically all high temperature conditions the process is well into the fall-off region. Thus it is necessary to determine a collision efficiency. Unfortunately, the lower temperature measurements on the pressure dependence cannot be fitted within the framework of RRKM theory. This leaves predictions of high temperature behavior very uncertain. The situation with respect to phenyl and benzyl radical is not completely clear<sup>18</sup>. They may be so stable that in most systems decomposition may not be an important destruction channel. This is probably the case for propargyl. The rate expression for the decomposition of allyl radical to form allene and hydrogen atom<sup>5</sup> have recently been determined. The rate expression consistent with the low temperature rates for the reverse reaction is  $5 \times 10^{13} \exp(-29500/T) \text{ s}^{-1}$ . This can be compared with a rate expression of  $4 \times 10^{13} \exp(-19000/T) \text{ s}^{-1}$  for the comparable decomposition of isopropyl radical. There is thus over 20 kcal/mol difference in activation energy and is in fact much larger than the difference in that for C-H bonds in ethylene and ethane. On a per hydrogen basis the A-factor is somewhat larger and is consistent with the "stiffer" allyl as compared to alkyl radicals. In the case of butenyl-2, from the reaction of hydrogen with butadiene it is possible to derive the rate expression  $4 \times 10^{13} \exp(-24200/T) \text{ s}^{-1}$ . It would appear that the resonance energy is almost fully expressed in the activation energy of the decomposing species. Butenyl-3 contains a beta C-C bond that is adjacent to the double bond and a beta C-H bond that is also allylic. For alkyl radicals beta C-C bond cleavage is always the preferred decomposition mode. There is need for data on this and related unsaturated systems such as butadienyl. The branching ratio for C-C and C-H bond cleavage have important consequences on models for the building of the larger unsaturated structures during hydrocarbon decomposition.



Larger alkyl radicals can readily isomerize through hydrogen migration. Transfer between the 1,4 and 1,5 appear to be more facile than the 1,2 and 1,3 reactions. At 1100 K contributions from the latter have been noted. Similar processes can occur for the unsaturated counterparts. In addition the latter can also cyclize. Thus 4-pentenyl-1 can cyclize to form the cyclopentyl radical<sup>5</sup>. There are large uncertainties in the rate expressions for such processes. Activation energies are expected to be low or in the 20 kcal/mol range and A-factor should reflect a "tight" transition state. This leads to major uncertainties in the nature of the breakdown products of the larger unsaturated molecules and is an important barrier in tracing the breakdown pathways of hydrocarbons in high temperature systems.

For high temperature unimolecular processes, it is necessary to consider at all times the effect of fall-off. In general, existing data can be fitted within the framework of RRKM calculations. The problem with vinyl mentioned earlier is probably the only exception. The requirements for making correct predictions are accurate high pressure rate expressions and the average energy transferred per collision and is particularly important for the estimation of branching ratios. This has been discussed earlier for propene decomposition. Low activation energy decomposition processes may have additional complications at high temperatures since a steady state distribution may not be achieved. Thus the standard treatment is not adequate and the solution of non-steady state master equation is required. Programs to carry out such calculations are now beginning to appear. It would be interesting to test such procedures with careful experiments.

#### Radical Attack

The weakness of the allylic and benzylic C-H bonds leads naturally to the assumption that rate constants for abstraction processes resulting in the formation of resonance stabilized species will be vastly enhanced over that for alkyl radicals. This is not the case and is demonstrated in Figures 2 and 3 where the comparison is for the abstraction of benzylic and allylic hydrogens by hydrogen and methyl and the corresponding alkane, propane. It will be noted that the 10-11 kcal/mol difference in the bond being broken if directly manifested in the activation energy would have led to differences of 2 orders of magnitude at 1100 K and 4 orders of magnitude at 550 K. Instead, in the case of abstraction by methyl it is apparent that the rate constants on a per hydrogen basis are commensurate with that from an secondary hydrogen. For abstraction by hydrogen atoms, rate constants on a per hydrogen basis are only a factor of 2 larger than that for the normal hydrogens and not even as large as that for a secondary hydrogen. It will be recalled that the difference in bond energies between primary and secondary hydrogens in alkanes is about 2 kcal/mol. These results are consistent with a transition state that is similar to the reactants and contrasts with the situation for unimolecular decomposition where the resonance energy is fully manifested. Consistent with the former is the relative constancy in the rate constant for the abstraction of benzylic and allylic hydrogens. These observations also can serve as a basis for prediction of abstraction rate constants for other reactions that lead to resonance stabilized products.

Through detailed balance one can then calculate the rate constant for

abstraction by resonance stabilized species. Due to the resonance destabilization of the bond this is an endothermic process. Since this is not made up by a faster abstraction rate constant in the forward direction, abstraction by resonance stabilized radicals must be quite slow. The consequence is that such species can cause chain termination through combination with other radical processes present in the system.

In the case of a vinylic C-H bond, the increase in bond strength appears to be manifested in the form of a smaller rate constant for the abstraction process. This can be seen in Figure 3, where the recent data for methyl abstraction<sup>20</sup> of a vinylic hydrogen from ethylene can be compared with the molecules discussed earlier. There are virtually no other reliable data on the rate constants of abstraction by vinylic or phenyl radicals. Since such processes are all more exothermic than comparable processes by methyl, it is very tempting to use the results from methyl as a lower limit.

Radicals can add to a site of unsaturation. In many instances this is a reaction that has no effect. For example terminal addition of H-atom to propene will lead to the formation of isopropyl radical which will readily go back to propene in high temperature systems. Terminal addition is the observed addition mode at room temperature. It has recently been found that the preference for terminal addition is mainly an enthalpic effect and is related to the stability of the radical that is formed<sup>21</sup>. Thus as the temperature is increased non-terminal addition becomes increasingly important. Non-terminal addition by hydrogen to a compound such as propene will lead to the formation of n-propyl radical which will decompose to form propene and methyl. The effect is that of a displacement reaction. Should the general trend hold then terminal addition to butadiene will be overwhelmingly favored and the induced decomposition by hydrogen atom to form vinyl and ethylene cannot be an important process. Addition processes, even at the non-terminal position have lower activation energies than the competitive abstraction processes. The A-factors are however lower. It is thus important at lower temperatures. Figure 4 summarizes data on hydrogen attack on isobutene and toluene<sup>22-23</sup>. It is clear that hydrogen addition to the olefin is favored over that for the aromatic. The overall effect of these processes is to remove the side chains from the unsaturated structure.

Resonance stabilization renders organic radicals much less thermally and chemically reactive. Thus it is expected that their steady state concentrations will be much larger. Reaction with itself and other organic radicals will then become important. The rate constants for such process are not much different than that of the non-resonance stabilized species. These radicals will also add to unsaturated compounds. As the temperature is increased the reaction will be reversed. The newly formed radical can also isomerize or cyclize. As a result one has a chemical activation system involving low activation energy process. There has been considerable recent work involving vinyl and phenyl addition to unsaturates<sup>24</sup>. As in the case for the resonance stabilized case these may be reversible. Alternatively the addition may be followed by ejection of a fragment of the original molecule. The results must then be treated in terms of a chemical activation process. Such treatment is handicapped by the fact that the experimental results are really a combination of several elementary single step processes. Without the rate expressions for the true elementary steps extrapolations and predictions may be unreliable.

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Table 1: Rate expressions for various bond breaking processes(1100K).

$k(\text{hexane} \rightarrow 2\text{propyl}) \rightarrow 2.5 \times 10^{16} \exp(-41000/T) s^{-1}$   
 $k(\text{hexene-1} \rightarrow \text{allyl} + \text{propyl}) \rightarrow 8 \times 10^{15} \exp(-35600/T) s^{-1}$   
 $k(\text{hexyne-1} \rightarrow \text{propargyl} + \text{npropyl}) \rightarrow 8 \times 10^{15} \exp(-36300/T) s^{-1}$   
 $k(1,7\text{octadiene} \rightarrow 4\text{-pentenyl} + \text{allyl}) = 1.2 \times 10^{16} \exp(-35700/T) s^{-1}$   
 $k(1,7\text{octadiyne} \rightarrow 4\text{-pentynyl} + \text{propargyl}) = 1.6 \times 10^{16} \exp(-35760/T) s^{-1}$   
 $k(1,5\text{hexadiene} \rightarrow 2 \text{ allyl}) = 7 \times 10^{14} \exp(-29500/T) s^{-1}$   
 $k(n\text{-phenylbenzene} \rightarrow \text{benzyl} + \text{nbutyl}) = 1 \times 10^{16} \exp(-36500/T) s^{-1}$   
 $k(1\text{-phenyl-1-pentene} \rightarrow 3\text{-phenyl-2-propenyl} + \text{ethyl}) = 3 \times 10^{15} \exp(-33800/T) s^{-1}$

Table 2. Rate expressions for the decomposition of unsaturated compounds into molecular entities

$$\begin{aligned}
 k(\text{hexene-1} \rightarrow 2\text{propene}) &= 4 \times 10^{12} \exp(-28900/T) \text{ s}^{-1} \\
 k(1,7\text{-octadiene} \rightarrow 1,4, \text{pentadiene} + \text{propene}) &= 3 \times 10^{12} \exp(-27900/T) \text{ s}^{-1} \\
 k(1\text{-hexyne} \rightarrow \text{allene} + \text{propene}) &= 5 \times 10^{12} \exp(-28400/T) \text{ s}^{-1} \\
 k(6\text{-methylheptyne-2} \rightarrow 1,2\text{butadiene} + \text{isobutene}) &= 2 \times 10^{12} \exp(-28700/T) \text{ s}^{-1} \\
 k(1,7\text{octadiyne} \rightarrow \text{allene} + \text{pent-1-ene-4-yne}) &= 5.6 \times 10^{12} \exp(-27860/T) \text{ s}^{-1}
 \end{aligned}$$

Figure 1. Typical Bond Dissociation Energies for alkanes, alkylbenzenes, alkenes and alkynes.

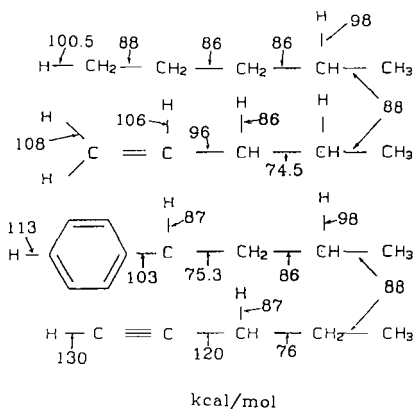


Figure 2. Rate constants for 1-hexene and 1-hexyne decomposition through bond breaking and retro-ene reactions.

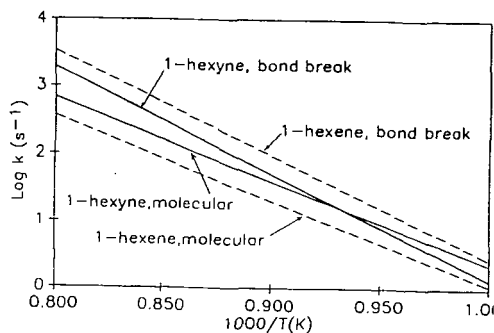


Figure 3. Rate constants for abstraction of hydrogen by hydrogen leading to benzyl, allyl, n-propyl and isopropyl radicals. [per hydrogen basis]

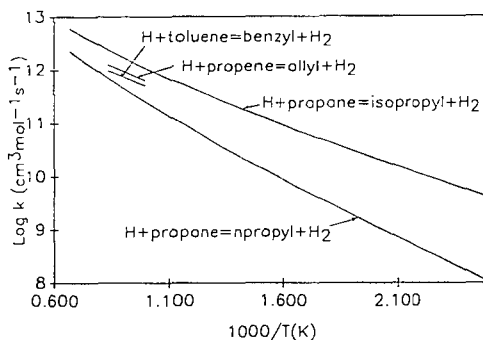


Figure 4. Rate constants for abstraction of hydrogen by methyl leading to benzyl, allyl, vinyl, isopropyl and n-propyl radicals. [per hydrogen basis]

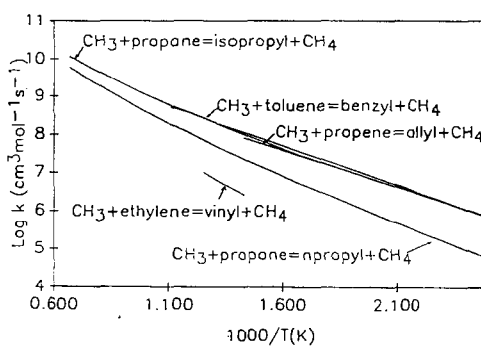
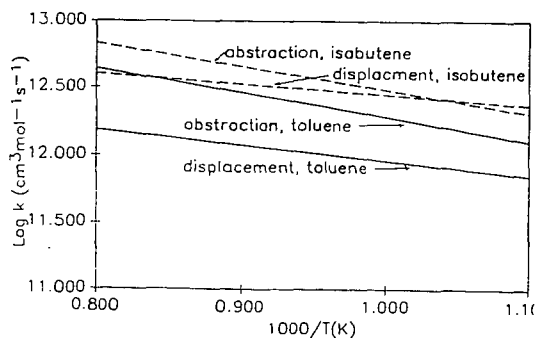


Figure 5. Rate constants for hydrogen atom attack on isobutene and toluene.



## AUTORADIOGRAPHIC AND HYDROTHERMAL PROBES OF INTERFACIAL CHEMISTRY IN OIL SHALE AND COAL

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Keywords: hydrous pyrolysis, autoradiography, maturation

### INTRODUCTION

The chemistry leading to the formation of petroleum hydrocarbons is an area of considerable interest, and major progress in our understanding has evolved in widely ranging studies over the past 25-30 years. The advances are due in large part to a broadening interest in the problem, encompassing large portions of the geochemistry, coal chemistry, and chemical kinetics communities, and to the development and application of new and sophisticated instrumentation.

However despite these advances, it is clear that there are still sizeable gaps in our perceptions of the processes, extending down to a very fundamental level. Thus for example, while the formation of petroleum is normally thought to be a geologically lengthy process involving the diagenetic breakdown and maturation of accumulated organic matter, it has been recently shown that petroleum hydrocarbons can be formed in much shorter periods of time in sedimented, submarine rift basins at 280°-350°C (Simoneit, 1985; Simoneit, et al., 1987). The products include an *n*-alkane distribution typical of petroleum, and highly condensed polynuclear aromatic hydrocarbons (PAHs) including phenanthrene, pyrene, benzpyrenes and coronene. The alkane origins are unclear, as are those of the PAHs, which are commonly observed as products of hydrocarbon pyrolysis only at temperatures above 550°C, while coronene itself is not generated at temperatures below 650°C (Commins, 1969). These temperatures are obviously far greater than those in the vent region, and the observations reflect the operation of largely unexplored but significant chemical processes.

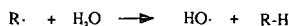
One of the tools widely used in maturation studies is hydrous pyrolysis, or the heating of immature sediment in liquid water at pyrolytic conditions at 290-360°C (Lewan et al., 1979; 1981). (The critical temperature of water is 374°C.) The process is thought to accelerate maturation so that hydrocarbon development can be examined in a laboratory setting, although the claim that the procedure exactly mimics the natural process has been questioned (Monthieux et al., 1985; Tannenbaum and Kaplan, 1985; Comet et al., 1986).

Whatever the case, the chemistry of very hot water at the organic-mineral boundary is central to question of hydrocarbon production. Specific key issues are the nature of bonding at the interface, and effects of water in the hydrothermal regime on the chemistry. The discussion here offers some thoughts on those questions, drawing upon both our interpretation of hydrous pyrolysis data by Hoering (1984), and our work on organic/mineral interfacial interactions.

### BACKGROUND

In studies of maturation it has been shown that the presence of liquid water increases the pyrolysate yield (Comet et al., 1986) and minimizes or eliminates the high olefin yields seen in dry pyrolysis (Hoering, 1984). It is often suggested that the key role of water in

hydrous pyrolysis is to cap pyrolytically formed organic free radicals (Monthioux et al., 1985; Hoering, 1984; Comet et al., 1986).



However this reaction is endothermic by 25-30 kcal/mol, and cannot be significant at hydrous pyrolysis temperatures. We have recently pointed out that if free radical chemistry is significant in hydrous pyrolysis, a more likely route is rapid, initial ionic deuterium-protium exchange between  $D_2O$  and a phenol, a thiol, or  $H_2S$ , followed by deuterium atom transfer to organic free radical sites (Ross, 1992).



On the other hand there is no compelling evidence at present supporting any specific mechanistic route.

Nonetheless some sense of the sequence for hydrocarbon production can be developed with attention to the hydrous pyrolysis work by Hoering (1984). He reported on the treatment of finely divided samples of Messel shale with  $D_2O$  at 330°C/3 days, under which conditions about 8% of the organic carbon was recovered as a mixture resembling petroleum hydrocarbons. The recovered products included a series of *n*-alkanes over the range  $C_{14}$ - $C_{30}$ , with each alkane itself comprised of a broad distribution of isotope isomers containing 0 to more than 14 deuterium atoms. The D-isomer distributions were all very similar, with the maxima spanning  $D_3$ - $D_6$  for the various alkanes, and with no apparent trend. Preexisting alkanes and olefins were ruled out as the source of the products by using source rock that had been previously extracted. The possibility that trapped alkanes surviving prior extraction were sources was eliminated in control experiments in which the source material was spiked with *n*-octadecane, which which then recovered after treatment with a considerably lower deuterium content than had been noted for the kerogen-derived material.

A particularly meaningful result was from work in which the starting shale was spiked with the olefin *n*-octadecene. Fully 60% of the olefin was recovered as the corresponding *n*-alkane, a result demonstrating the significant reduction potential available at hydrous pyrolysis conditions. Indeed, hydrogen is a common gaseous product in hydrous pyrolysis experiments (Lewan et al., 1979; 1981). The recovered alkane in this case contained deuterium, although the distribution was different from that found in the kerogen-derived alkanes. These results are discussed more fully below.

## RESULTS AND DISCUSSION

### Hydrous Pyrolysis and Deuterium Distribution

In considering Hoering's results, we seek to reconcile the data with a simple reaction model.\* The development here is primarily qualitative, and our goal is the simple compari-

\* A preliminary version of this work has recently appeared (Ross, 1992).

son of calculated and observed isotope isomer distributions. Detailed, quantitative reaction kinetics will be considered in a later development.

The basis of the process is the output from an integration routine based on the Gear algorithm (Moore and Pearson, 1981) and operated on a VAX 11/750 computer. The operation numerically simulates the sequential exchange in (1), presuming identical



rate constants for each step. (The kinetic isotope effects at these temperatures should be insignificant.) The output is a series of D-isomer profiles, with the major isomer moving to increasing substitution with time.

The deuterium contents in the alkanes recovered by Hoering in the alkane-added, the olefin-added, and the straightforward hydrous pyrolysis experiments are shown in Table 1. The table shows first that while the isotope substitution in the alkane-added experiment is small, there is nonetheless almost 30% exchange. Thus the *n*-alkane is not unreactive toward exchange in the system. In addition, in the face of a large excess of D<sub>2</sub>O, 9% and 4-6% of the olefin- and kerogen-derived alkane are D<sub>0</sub> respectively. These values are not insignificant and suggest that reduction of olefin from a strictly protio source precedes exchange, which then operates on the D<sub>0</sub> alkane.

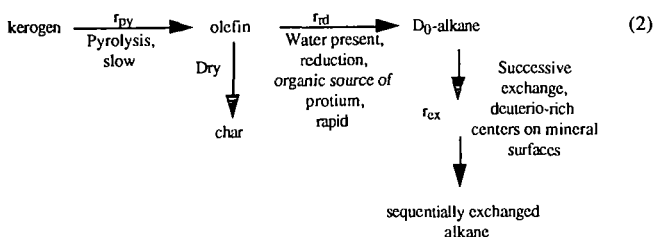
Next, the D/H ratios show that despite their similar %-D values, the kerogen-derived alkane has experienced far more exchange than has the alkane recovered from the olefin-added study. This difference is displayed in Figure 1a which shows the isomer data for the kerogen-derived *n*-heptadecane, and in 1b which presents the distribution for the *n*-octadecane from added *n*-octadecene. In the former the distribution peaks at D<sub>3</sub> and extends to isomers beyond D<sub>14</sub>. In contrast the 1b peaks at D<sub>2</sub>, and no D-isomer is reported beyond D<sub>10</sub>.

Also presented in the figures are the predicted distributions based on eq (1), starting with the D<sub>0</sub>-isomer, and adjusted to peak respectively at D<sub>3</sub> and D<sub>2</sub>. Clearly in 1a the observed distribution is far broader than the calculated one; there is both far more D<sub>0</sub> and significant isotope substitution beyond D<sub>8</sub> in the recovered product than predicted in the simple statistical model. A similar lack of fit is observed for the other *n*-alkanes recovered in the work.

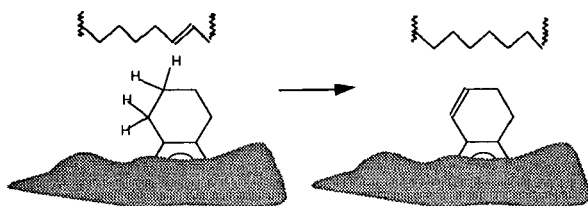
The match in 1b on the other hand is very good. The added olefin obviously behaves differently from thermally generated, kerogen-derived alkane precursors. It must be quickly reduced to the protio alkane, which then exchanges as in eq (1).

Accordingly, to explain the generation of alkane from kerogen, the thermal generation of olefin must be included in our considerations, as shown in the scheme in (2). The scheme includes separate pyrolysis, reduction, and exchange steps, and a branching step for dry pyrolysis to be discussed below. Since the olefin reduction is rapid,  $r_{rd} \gg r_{py}$ , the rate of alkane production is essentially the pyrolysis rate. We presume the reduction step to proceed necessarily by way of reaction with the nonexchangeable protium in the organic





phase, i.e.



while exchange must take place on the mineral surfaces which have been equilibrated with  $\text{D}_2\text{O}$ .

We can next consider a selection of scenarios in which the ratios  $r_{\text{py}}/r_{\text{ex}}$  are varied over a range of values (Figure 2). The *n*-heptadecane profile is also shown in the figures. They show that for a fixed exchange rate a relatively high alkane production rate provides a distribution shown in 2a like that in 1a except in this case the peak is at  $\text{D}_6$ . Reducing the ratio by an order of magnitude rolls the peak down to lower D-values, and provides a satisfactory fit to the observed profile as shown in 2b. Decreasing the ratio still further in 2c yields a profile favoring the low-D side, as would be expected as the conditions shift toward what is effectively a large reservoir and a steady-state supply of precursor.

The match in 2b supports the sense of the scheme in eq (2) that alkane precursor supply is not instantaneous, but with a rate comparable to that for exchange. Thus for the Hoering work,  $r_{\text{rd}} \gg r_{\text{py}} = r_{\text{ex}}$ . A key aspect of this exercise is the comparison of figures 1b and 2b, for which the ratio of exchange rates necessary for the observed fits,  $r(2b)_{\text{ex}}/r(1b)_{\text{ex}}$ , is about 3. This result is in line with the difference in the H/D ratios for the olefin-added and kerogen-derived alkanes in Table 1. Since the exchange is mineral surface promoted, these data reflect an extensive association of the kerogen with the mineral surface in the source rock, and extensive chemistry specific to the interface.

#### Autoradiological Probe of the Mineral/Organic Boundary

It is recognized that silica surfaces bind hydrocarbons in what must be donor-acceptor complexes (Iler, 1979). Similarly, oxygen-containing compounds including benzoates, phthalates, salicylates, phenols, and catechols complex with aluminum oxides and hydrox-

ides (Davis and Hem, 1989). However little is known about the interactions at the phase boundary and the nature of the bridging structures.

In recent studies directed at the formation and durability of asphalt-aggregate bonds in highways we have developed some relevant data using tritium-tagged organics and autoradiographic techniques as sketched in Figure 3 (Ross, et al., 1991). Clean surfaces of several aggregate samples were exposed to very dilute solutions of the compounds 4-HO<sub>2</sub>C-C<sub>6</sub>H<sub>5</sub>(CHT)<sub>2</sub>(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub> (I) and C<sub>6</sub>H<sub>5</sub>(CHT)<sub>2</sub>(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub> (II) in refluxing toluene (111°C/~30 min).<sup>\*</sup> The samples were then extracted with toluene in a Soxhlet (20 hr), and the flat surface was mated to fast photographic film. Following 8-day exposures the samples were extracted with water in a Soxhlet (100°C/2 hr), and photographed again.

The results for a rock sample containing primarily silica and K-feldspar (potassium aluminosilicate) treated with the carboxylic acid (I) are presented in Figure 4. The images in 4a and 4b show the results following the toluene and water extractions, respectively, and both show remaining organic material in a mosaic of distinct bonding and nonbonding zones. 4b is less intense than 4a, a significant result demonstrating the removal of some but not all of the material.

This result cannot be reconciled with simple acid-base association between (I) and the surface since such complexing would be fully destroyed by water. It is recognized that benzene yields a carbonaceous film on clean platinum surfaces at around 100°C (Davis and Somorjai, 1980), and aluminosilicates engage in similar activity (Somorjai, 1991). However the phenomenon has received little study, and little is known about the nature of the films nor of their bonding to the mineral surface. We surmise that the tritium-containing substances bound to the mineral surface are residues from surface promoted decomposition, and are very strongly bound to the surface.

The character of the sites associated with the films is revealed in SEM/EDAX studies of the same rock surface presented in Figure 5. 5a is an enlarged portion of 4b (top, left of center), and 5b is the SEM image of that region at about 50 x magnification. K and Si maps of the same region are shown in Figures 5c and 5d, respectively; Ca, Al, and Fe maps were also prepared but are not shown. The figure shows the Si distribution to be uniform over the region, as are the Ca and Fe distributions although they show a lower density of spots. The K and Al maps, however, shows distinct patterns of K-rich and -poor regions, which are, respectively, feldspar, a potassium aluminosilicate, and silica.

Comparison of the image in Figure 5a and the K map in Figure 5c shows an unmistakable similarity in patterns. This match demonstrates a preferential reactivity of, and bonding to, the feldspar regions of the rock. Examination of the SEM image of the surface in 5b shows a faint pattern also matching the K map. Such patterns are not visible in aggregate that has not been treated, and reflect the deposition of the film in the active regions.

Subsequently the unsubstituted arene II was studied with aggregate samples that were virtually fully silica, and provided faint but well defined images faithful to the exposed silica surface following the toluene-stripping (not shown). Water-stripping in this case eliminated all trace of the signal. There is little doubt that the silica surfaces in the studies with I show some signal; however it is difficult to be observed because of the much stronger response in the feldspar regions. This result, a carbonaceous film surviving 20 hr of toluene extraction derived from an organic compound with not polar functionality on a relatively unreactive surface, demonstrates the likely ubiquity of these films, and their possible significance in source rock and the maturation process.

<sup>\*</sup> The solutions also contained asphalt, an aspect of the work not important to the discussion here.

## CONCLUSIONS

The action of water at the organic-mineral interface is apparent from the diminishing signal in Figures 4a and 4b. The water in some manner strips some of the organic material from the surface. It is conceivable that the stripping involves hydrolysis of the mineral phase supporting the organic film rather than action at the bonds bridging the two phases. Whatever the specific mode of action, the process should be important in hydrous pyrolysis in separating the two phases.

This activity goes hand in hand with the moderation of the acidity of mineral sites by water, as recognized by Tannenbaum and Kaplan (1985). Acidic sites on clay surfaces have been invoked as a significant feature of maturation (Alexander, et al., 1982, 1984), and water must therefore be significant to the degree and direction of that chemistry. We have utilized these views in eq (2), suggesting that in the absence of water the high surface acidity irreversibly reincorporates the pyrolytic products into the organic phase as char.

Thus since aromatization is a major driving force during maturation (Hayatsu et al., 1987), and therefore a source of hydrogen (or reduction potential), we can envision a system which in the absence of water the organic phase remains associated with the mineral phase, and thermolytically releases hydrogen and relatively small quantities of olefin. The major product is an H-poor char on the surface. In contrast when water is present, the phases are separated, the moderated surface acidity reduces char formation, and the olefins are available for reduction to alkanes. The alkanes then engage in hydrogen exchange with other appropriate sites on the mineral surface before escaping into the aqueous medium, which at near critical temperatures is a good alkane solvent (Skripka, 1979).

## ACKNOWLEDGEMENT

It is a pleasure to acknowledge very useful discussions of hydrous pyrolysis with my colleagues Dr. Donald McMillen and Dr. Ripudaman Malhotra. Dr. McMillen was helpful in clarifying the important issue of a mixed ionic/free radical sequence for protium/deuterium exchange, and Dr. Malhotra emphasized the point that slow kerogen thermolysis could be significant in the product isomer patterns.

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Table I

D-Introduction into Recovered Alkane<sup>a</sup>

	From added <i>n</i> -octadecane	<i>n</i> -Octadecane from added octadecene	Kerogen-derived <i>n</i> -C <sub>17</sub> - C <sub>29</sub>
%-D-containing <sup>b</sup>	28	91	94-96
D/H	0.02	0.09	>0.20 <sup>c</sup>

a. From Hoering, 1984

b. Fraction of recovered alkane with at least one deuterium atom.

c. The D-quantities were not presented beyond D<sub>14</sub>, but the exchange pattern suggests significant contribution by more highly exchanged isomers. The D/H value is thus a lower limit.

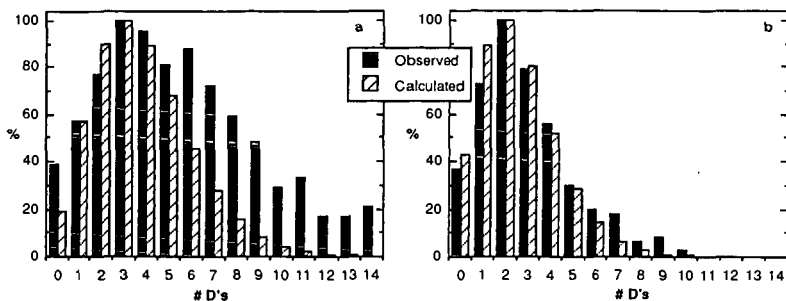


Figure 1. a) D-distribution for kerogen-derived heptadecane and calculated profile.  
b) D-distribution for octadecene-derived octadecane and calculated profile. In both cases the calculation is for simple exchange via eq. 1.

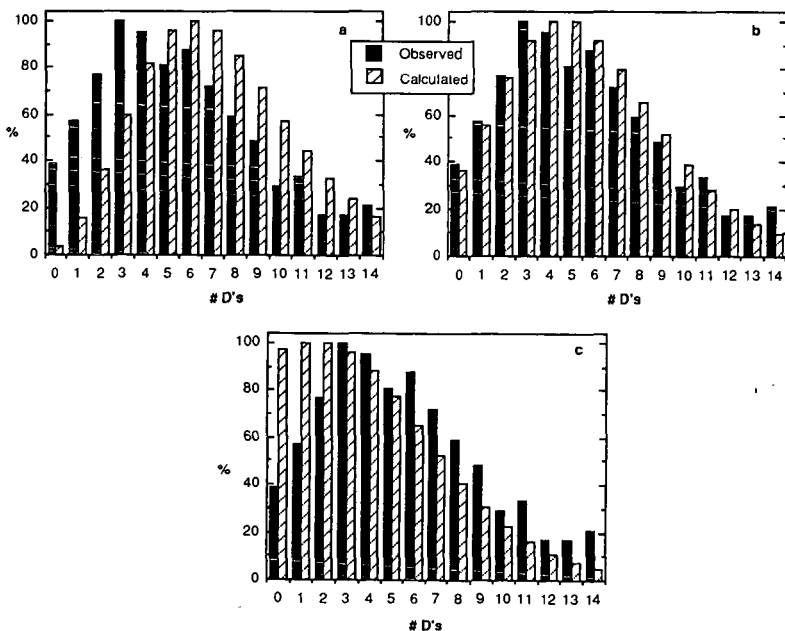
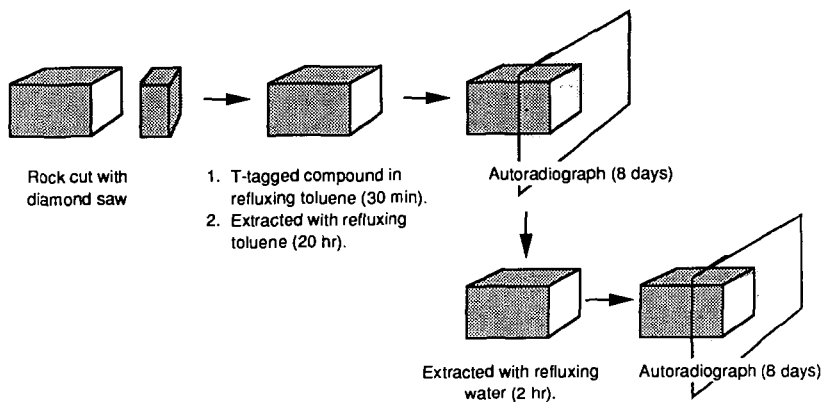
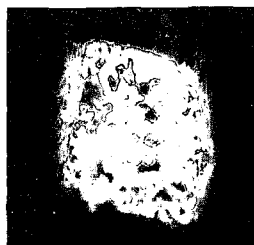


Figure 2. D-profile for kerogen-derived heptadecane and calculated profiles via eq. 2.  
a)  $r_{py}/r_{ex} = 4.60$  b)  $r_{py}/r_{ex} = 0.46$  c)  $r_{py}/r_{ex} = 4.6 \times 10^{-2}$



CAM-2847-2

Figure 3. Sequence for autoradiographic study.



(a) AR image after toluene-stripping



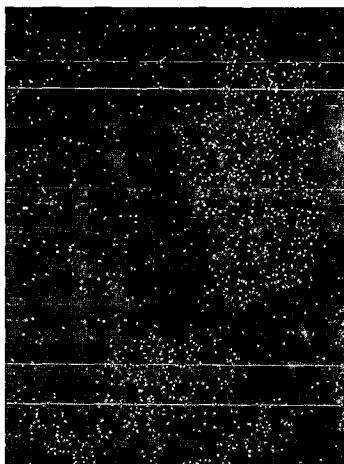
(b) AR image after water-stripping

CPM-2847-1

Figure 4. Autoradiograph images following treatment with  $\text{HO}_2\text{C-Ar(CHO)}_2(\text{CH}_2)_{10}\text{CH}_3$ .



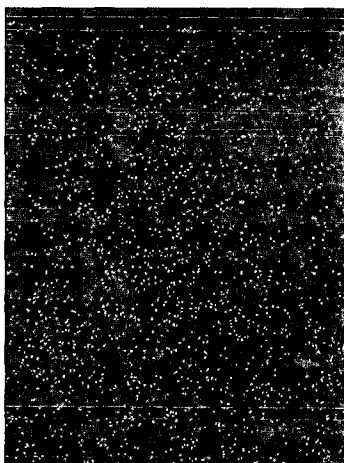
(a) AR Image



(c) K Map



(b) SEM Image



(d) Si Map

RP-8674-8A

Figure 5. SEM/EDAX studies of test piece with carboxylic acid.

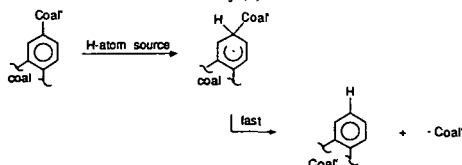
## HYDROGEN-TRANSFER IN RETROGRADE REACTION -- THE HERO AND THE VILLAIN

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**Keywords:** Liquefaction Mechanism, Hydrogen-Transfer, Bond-Cleavage, Retrograde Reaction.

### INTRODUCTION

Much attention has been focused over the years on the nature of the bond cleavage that takes place during coal liquefaction, pyrolysis, and combustion. Owing to the essential impossibility of determining the "critical" linkages between clusters in the organic structure of coals, much of what we now "know" has only been inferred from comparisons between coal behavior and that of model compounds or probe molecules. Nevertheless, it is now generally recognized that a picture of this bond cleavage that involves only the spontaneous thermal scission of weak bonds is, at best, incomplete and that the cleavage of strong bonds as a result of hydrogen-transfer should be included in our picture of coal conversion chemistry (1).



Scheme 1. Cleavage of strong bonds engendered by H-transfer to ipso position.

Recognition of the fact that hydrogen-transfer is a *prerequisite* to strong bond cleavage (rather than merely a subsequent step necessary to limit recombination) leads, via consideration of microscopic reversibility, to the conclusion that hydrogen-transfer is also a prerequisite to the *formation* of strong bonds, or retrograde reaction. Tracing Scheme 1 backwards, for instance, the link between Coal and Coal\* is not "locked" into place until some agent removes the ipso H-atom in what amounts to the reverse of the first step. Thus, the task of increasing coal liquefaction yields may in some cases involve the dilemma that introduction of a particular H-transfer agent will increase bond *formation* as well as bond cleavage. It follows then that the relative utility of various H-transfer agents in liquefaction cannot be truly understood unless we know their proclivity for promoting both bond-cleavage and bond-formation. This paper is an attempt to assess the various categories of coupling reactions that may constitute the retrograde processes limiting coal conversion yields and their sensitivity to changing reaction conditions.

Although the importance of retrogressive reactions has become more obvious through careful studies of liquefaction kinetics and products, the fundamental chemical reactions and their kinetics have remained obscure. For instance, researchers such as Neavel recognized some time ago that soluble products could be generated and consumed very rapidly under coal liquefaction conditions (2). Similar observations have been made for pyridine solubles under pyrolysis conditions, where there is no added solvent (3). In a sense the whole technology of heavy oil conversion is bound up with retrograde reactions, in that thermal treatment of petroleum asphaltenes under a variety of conditions can produce similar amounts of distillate, but the amount of retrograde product (coke) generated in conjunction with these volatiles is critically dependent on conditions of catalyst, medium, and hydrogen pressure (4-5). Thus the impact of retrograde processes can be quite obvious, but the detailed nature of the responsible bond forming reactions is unclear.

In order to provide a background for better addressing retrograde reactions, we have examined the literature for evidence of retrograde reactions not only in actual coal conversions, but in studies of model compounds, probe molecules, and grafted-probes, and have tried to extend our understanding of the bond-forming chemistry in some of these circumstances by mechanistic numerical modeling. This model was chemically detailed, but structurally limited -- not intended in any way to actually model the conversion of a real coal, but to ascertain how chemical factors influence certain classes of reactions under different circumstances.



This modeling incorporates the most basic of the bond cleavage types now thought to be important in coal liquefaction, and its validity is dependent of course on the appropriateness of the reactions considered. In this paper we summarize some of the results of this literature scrutiny and modeling effort.

## RESULTS AND DISCUSSION

**Pyrolysis of Grafted Coals.** Zabransky and Stock have covalently grafted various groups to an Illinois No. 6 coal through various C-O and C-C linkages and pyrolyzed these coals using a resistively heated wire grid reactor (6-12). Through isotopic labeling of various carbons and hydrogens in the grafted groups, followed by mass spectrometric analysis of the gaseous products, identifiable portions of the grafted structures were tracked with a degree of certainty that is not achievable with unmodified coals. These studies have allowed the authors to reach a number of interesting conclusions regarding the nature of bond cleavages in structures typified by the grafted groups. Here we wish to focus instead on what limits this cleavage, specifically on how retrograde reactions compete with the bond scission processes.

Some indication of the severity of retrogression can be seen from the products reported by Zabransky and Stock (6-12) for pyrolysis of deuterium- and  $^{13}\text{C}$ -labeled O-n-propyl, O-nC<sub>18</sub>H<sub>37</sub>, O-CH<sub>2</sub>CH<sub>2</sub>Ph, and O-CH<sub>2</sub>Ph Illinois No. 6 coals. Selected results are shown in Table 1, derived from their data.

The authors have discussed the extent to which the results reveal that the cleavage of strong bonds by  $\beta$ -scission, following either H-abstraction from an alkyl group or H-transfer to an aromatic group, are important routes for fragmentation of the grafted structures. They conclude, for instance, that the abstraction route for the aliphatic portion of alkylaromatic structures tends to be more facile than the ipso-addition route; at least when the aromatic is a single phenyl ring. These pathways account for cleavage of 2 to 40% of the grafted groups (6,9). Just as important as determination of the modes of cleavage, however, is comparison of the yields of cleaved products with the inferred yields of uncleaved, or retrograde, products. Table 1 shows the percents of the grafted portions that are converted to various cleavage products, as determined by isotopic labeling. Though the heavier products were not fully analyzed, and high precision was difficult to achieve on the scale of the experiments, the general trend is clear: substantially less than half of the grafted groups were evolved, via either weak bond thermolysis or induced scission of strong bonds, during pyrolysis to final temperatures generally in the 750 to 850°C range. This observation becomes still more striking when the rate of thermolysis of the O-C linkages in the various graftings are considered.

Table 2 shows estimated rates of cleavage for various final pyrolysis temperatures, and also the fractions of the linkage expected to be still intact by the time a particular temperature is reached (at the 1000°C/s heating rate used in the pyrolysis experiments). To take into account cage recombination, the last three columns in Table 2 are estimated by assuming that 99% of the radicals produced by thermolysis recombine before they can escape the cage, in effect extending the life of the weakly bonded species by a factor of 100 [SSD85].

The slowest homolysis is of course expected for the O-alkyl grafts, in which the O-C bonds are about 10 kcal/mol stronger than any of the O-arylmethyl cases (14). Even for this most strongly bound group, pyrolysis to a final temperature of 750°C (with zero hold-time), would leave an unconverted fraction of less than 1%, were there no recombination. However, if 99% recombination occurred in the cage, the fraction unconverted by 750°C would increase to 97%. Thus, for the O-alkyl grafted coals, the expected homolytic conversion of the graft to volatiles would critically depend on the extent of cage recombination. In contrast, the O-benzyl-type graftings have estimated homolysis rates that are higher by at least two orders of magnitude, and the fractions unconverted by 750°C would be no more than 4%, even assuming 99% cage recombination. Given this difference, it is striking that, in spite of having the slowest homolysis rates, the O-alkyl graftings are seen in Table 3-1 to have the highest fractional conversions to the corresponding alkane and its degradation products (~40%). For comparison, row 4 in Table 1 shows that only 8% of the weakly bound benzyl group of O-benzyl coal was detected as toluene. Clearly, the ease of conversion to volatile products in the case of alkyl structures is not dependent primarily on the ease of homolysis.

If the primary determinant of the extent of conversion of these weakly bound grafts is not the homolysis rate, then it must be either the rate of retrogression of these structures (including the fate of initially formed radicals), or the rate of the induced bond scission. For the case of O-nPr coal, Zabransky and Stock have shown (by examination of alkane/alkene ratios) that facile volatiles production with the O-nPr coal is not due to bond-scission induced by H-abstraction, but does indeed arise from homolysis (11,12). Thus, the conversion of O-propyl coal to aliphatic fragments is more complete than the conversion of O-benzyl coal to toluene, *in spite of* the fact that the former conversion occurs via a much slower homolysis. The successful homolysis of aliphatic linkages that are significantly stronger than the weak bond in the O-benzyl coal thus fixes the cause for the low yields of toluene on the proclivity of aromatic structures for undergoing retrograde reactions.

**Pyrolysis of Polymeric Coal Models.** More detail about the structural factors that facilitate retrograde reaction (other than the simple presence of aromatic groups) can be obtained from polymeric coal model studies. Several years ago, Solomon and Squire studied 27 polymers containing aromatic, hydroaromatic, and heteroaromatic groups linked together by ethylene, methylene, propylene, oxymethylene, ether, aryl-aryl, sulfide, and ester bridges (15,16), using the same heated-grid technique for the pyrolysis of the polymer models as was used by Zabransky and Stock used for their grafted coals. Because of limitations of space, we will merely summarize some of the conclusions that can be drawn from this study.

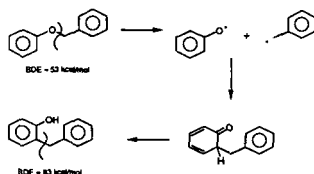
The primary focus of Solomon was on two-atom, i.e., weak linkages, for the reason that the traditional picture of thermal coal conversion chemistry then held that coal conversion resulted from spontaneous thermal cleavage (i.e., homolysis) of such weak linkages. However, precisely because most of the polymers consisted of low molecular weight clusters linked in linear chains by weak bonds, we find that the results offer a clearer view of the impact of retrograde reactions than they would with models containing some strongly linked clusters. These results reiterate some of the conclusions drawn from the grafted coal studies of Zabransky and Stock (6-12) and allow new ones to be drawn regarding the factors that limit the conversion of the polymers to volatiles. Among the most important of these conclusions are the following.

- Retrograde reactions profoundly limit volatile (or liquid) yields, which are controlled more by these coupling reactions than by the weakness of connecting bridges.
- Polymers or coal grafts containing aromatic components undergo retrograde reaction much more readily than aliphatic components.
- Increasing size of the aromatic clusters increases char yield, even under conditions where oligomer volatility limitations are unlikely to play a large role.
- As expected, the presence of hydroaromatic structure within the polymeric network decreases the retrograde reaction.
- Retrograde reactions tend to be worse for oxymethylene bridged polymers (particularly if in quinonoidal structures), notwithstanding an ~10 kcal/mol lowering of bond strength;
- Strengthening of weak ethylene bridges by removal of aliphatic hydrogen when there is no better source available contributes to char formation, but perhaps more importantly induces other crosslinking reactions to take place.

**Nature of the Retrograde Reactions.** From the studies highlighted above, together with related studies of coals and polymeric models and the work of Stein on the coupling of aromatics (17-21), we arrive at the following conclusions about the potential classes of retrograde reaction involving uncharged species in coal structures.

#### 1. Radical Recombination

- Resonance stabilized radicals -- Two resonance stabilized radicals can result only in the formation of weak bonds, providing only temporary retrograde products, *except* in the case of ring recombination of phenoxy radicals. The latter case can result in successful retrograde reaction because the highly unstable initial adduct is able to rapidly rearrange through facile inter-molecular proton transfer reactions that are known (22) to be accessible to phenolic structures at coal liquefaction temperatures *even* in hydrocarbon solvents.



Scheme 2. Formation of strong retrograde linkages by ring recombination of aryloxy radicals.

- Aryl radicals -- Recombination of two aryl radicals would produce a biaryl linkage, at ca. 115 kcal/mol the strongest C-C single bond possible in hydrocarbons; however, the reactivity of aryl radicals necessarily means their concentrations will normally be far too low to participate in cross-recombination reactions, let alone self-recombination reactions.

## 2. Radical Addition to Unsaturated Systems

- Aryl radicals -- Aryl radicals, if formed, are known to add readily to any other aromatic system. The strength of the new bond formed means that hydrogen is readily displaced, even in the gas phase (18,21), where the primary loss process available is direct unimolecular loss of H-atoms. In the condensed phase, where H-atom loss by radical disproportionation and radical hydrogen-transfer will be relatively much more favored, we would expect aryl radical addition to be essentially irreversible. That is, during coal liquefaction effective H-atom removal would be no problem and the principal factor limiting aryl radical addition will be the rate of aryl radical generation.
- Resonance stabilized radicals -- The addition of resonance stabilized radicals to aromatic systems constitutes the opposite extreme: the carbon-carbon bond formed will be at least 20 kcal/mol weaker than the C-H bond that needs to be displaced (13,14), i.e., direct addition-elimination or displacement of H atoms by resonance-stabilized radicals are much less favored. Such coupling requires "special" circumstance that are nonetheless present during much of the liquefaction process. These circumstances are either high concentrations of displacing radicals, the presence good leaving groups on these aromatic systems, extremely effective H-atom acceptors in the reaction mixture, or multiple opportunities for radical addition. In other words, coupling reactions of this type will be highly dependent on the nature of the H-atom removal agents.
- Molecular coupling -- Stein found it necessary to invoke direct bimolecular coupling of closed-shell aromatics to form biradicals in order to account for the coupling of anthracene (20). This reaction can be thought of as the addition of a highly unstable biradical; no bimolecular H-transfer process is fast enough to compete with the  $\beta$ -scission of the resulting biradical adduct to re-generate the two closed-shell aromatics. Adducts formed by such additions can evidently be stabilized only when geometrical factors favor very rapid *intra*-molecular H-atom transfer reactions.

## ASSESSMENT OF RETROGRADE REACTION BY MECHANISTIC MODELING.

In this section we summarize some results from use of a numerical reaction model (23) employing a surrogate coal structure to help address the factors controlling competing bond scission and retrograde reaction pathways during the initial stages of coal liquefaction. The addition of stabilized radicals was chosen as the retrograde reaction type, not because we believe it to necessarily be always the most important class of retrograde reaction, but because it is the class of bond-making reaction whose outcome is most likely to be sensitive to changing hydrogen-transfer conditions. The addition of resonance-stabilized radicals is highly reversible, such that if it results in successful formation of strong bonds between aromatic clusters, it will be because a very small fraction of a large number of original additions ultimately go on to stable products. For simplicity, we have limited the model to a pure hydrocarbon system, though the same general considerations will also apply to systems containing phenolics, where the presence of the -OH groups will in all likelihood further promote radical addition.

The model we have used is very detailed; it incorporates all relevant fundamental chemical reactions (non-ionic) of essentially all species, both closed shell and free radical, in the reaction system. Because of this detail, the model, of necessity, includes only a very limited set of starting structures. The model is homogeneous; it consists of relatively low molecular weight species assumed to be miscible in all proportions. We have made the simplifying assumptions that the system is free of concentration gradients and requires no mass- or heat-transport. The activity of  $H_2$  in solution is taken to equal that provided by presumed equilibrium with the gas-phase  $H_2$  pressure. This model was not intended in any way to actually simulate the conversion of a real coal, but to ascertain how chemical factors influence certain classes of reactions under different circumstances. There has been absolutely no attempt to force the model results to correspond to the phenomenology of coal liquefaction or pyrolysis.

Space prevents a full description of the model and results here; these details will be presented elsewhere (24). Given below is a brief summary of the results of the modeling as they apply to the prevention of retrograde

reaction. In some cases these results are a quantitative illustration of what could be qualitatively anticipated from thermochemical considerations. In other cases the results were qualitatively surprising.

- All scavengers that operate via a radical capping process have a dual role—they also act as initiators.
- "Scavengers" typically found to best aid coal conversion to volatiles or liquids appear to perform better because they are superior in some aspect other than scavenging.
- At short reaction times, where there is a large generation of fragment radicals from homolysis of the weakly bonded coal surrogate, modeling indicates that dihydroanthracene, as the better scavenger, indeed maximizes the yield of capped fragment radicals, and minimizes the yield of recombination products and radical displacement retrograde products.
- However, at long reaction times, the "better" scavenger actually *enhances* the yield of retrograde product. This is because, at longer reaction times when the burst of radicals from the decomposing coal has largely died away, the principal source of fragment radicals is abstraction of hydrogen atoms from the previously capped fragment species by the pool of scavenger radicals generated by the scavenger itself. Thus, the model elaborates a trend which has been noted previously (25), namely that coal conversion tends to be better in the presence of hydroaromatics that are not the best scavengers, and is evidently better because these latter scavengers tend to be better hydrogenolysis reagents, while being poorer radical initiators.
- Higher temperatures provide more reaction, but if there is not something to mitigate retrograde reactions, higher temperatures tend to cause the retrograde reactions to increase as fast or faster than the bond-cleavage reactions. This modeling result appears to be completely in accord with the common observation that increasing liquefaction temperature beyond about 440°C tends to lower coal conversion, and similarly in pyrolysis, that higher heating rates tend to decrease char yields, *primarily* when the higher heating rates are associated with more rapid removal of volatile products, (26).
- Under the conditions modeled, displacement of carbon-centered radicals from aromatic rings accounted for roughly four times as many retrograde products as did displacement of H-atoms
- The presence of H<sub>2</sub> does *not* inhibit retrograde product formation as much as it hydrogenolyzes retrograde products faster after they are formed. In fact, modeling indicates that H<sub>2</sub> can, at certain reactions times, *increase* the yield of retrograde products.
- The impact of added H<sub>2</sub> on hydrogenolysis (at least in the short term) does *not* come primarily through its maintenance of a useful hydroaromatic content, as has often been postulated in coal liquefaction, but through a higher steady state concentration of H• that is established long before the hydroaromatic content can be substantially affected.

### Summary and Conclusions

Our examination of literature data, together with thermochemical considerations and the associated numerical modeling of simplified reaction systems leads us to the following summary picture of retrograde reaction during coal conversion.

**Recombination with Phenoxy Radicals.** The major case where where radical recombination can lead to a true retrograde product is ring-recombination of a phenoxy radical with resonance-stabilized carbon-centered radicals. Studies with the model compound benzyl phenyl ether have shown that the presence of scavengers can decrease but cannot easily eliminate the formation of diarylmethane linkages though this route. We suggest that facile intramolecular proton-transfer efficiently converts the initially formed and unstable keto-form to the strongly bonded phenolic form. No such isomerization pathway is available for ring-recombination of two benzylic radicals.

**Dual Function of Radical Scavengers.** Modeling has illustrated the apparent paradox that the best scavengers may do the worst job of preventing radical addition. Hydroaromatic structures such as 9,10-dihydroanthracene that have very weak benzylic C-H bonds will also tend to have high steady state concentrations

of the  $\text{ArH}\cdot$  radicals generated in the scavenging act. Thus, the "better" scavengers may result in a lower steady state concentrations of candidate retrograde radicals *only* when the principal source of such radicals is something other than these abstractions, such as a rapid homolysis or  $\beta$ -scission. Accordingly, the concentration of resonance-stabilized radicals like benzyl and phenoxy can sometimes be decreased by scavengers, but they cannot be lowered below a minimum corresponding to the level that is generated by the hydroaromatic scavenger system functioning as an initiator.

Modeling also reveals that in many instances, the donor solvent content or  $\text{H}_2$  pressure do not serve so much to decrease the rate of retrograde product formation as to cleave such products after they have been formed. In fact, the presence of these reagents may actually *increase* the rate of retrograde product formation at certain times. thus, the major impact of  $\text{H}_2$  lies not in its scavenging ability, which is very modest, but in the fact that whatever scavenging does take place produces free H-atoms, which are highly active hydrogenolysis agents. This "direct" hydrogenolysis activity of free H-atoms is seen to be a much more important effect of  $\text{H}_2$ , at least at short reaction times, than the indirect effect of maintenance of donor level.

**Aryl Radical Addition.** Since aryl-aryl bonds are so strong, displacement of H-atoms by addition of aryl radicals is prevented primarily by minimizing formation of these radicals in the first place. Literature results suggest the somewhat counterintuitive observation that aryl radicals are generated principally by the much larger pool of (individually much less reactive) resonance stabilized radicals.

**Resonance Stabilized Radical Addition.** The displacement of C-H bonds by resonance stabilized radicals (whether acyclic and therefore leading to diarylmethane linkages, or cyclic and leading ultimately to biaryl linkages) will usually be dependent not only on the concentration of potential displacing radicals, but also on the facility with which the reaction system stabilizes the intermediate adduct by removing the hydrogen atom that is being substituted. For example, modeling indicates that retrograde products from homolytically generated benzylic radicals are lower when dihydroanthracene (rather than dihydrophenanthrene) is the hydroaromatic scavenger. However, at long reaction times, when the main source of benzylic attacking radicals is the radical soup itself, the higher radical concentration provided by the "better" scavenger acts to *generate* more attacking radicals and also to more readily stabilize the adducts through radical disproportionation. In addition, the very good H-atom accepting capability of anthracene itself also increases the fraction of the initial adducts that are successfully stabilized as retrograde products.

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
TABLE 1  
FATE OF STRUCTURES GRAFTED TO COAL VIA PHENOLIC OXYGEN:  
PYROLYSIS IN A HEATED WIRE GRID<sup>a</sup>

Grafted Structure	% of Graft Converted to		
	C <sub>1</sub> -C <sub>3</sub>	PhH	PhCH <sub>3</sub>
-nC <sub>3</sub> H <sub>7</sub>	1.7 C <sub>1</sub>	NA	NA
	9.1 C <sub>2</sub>		61
	28 C <sub>3</sub>		
-nC <sub>18</sub> H <sub>37</sub>	7.2	NA	NA
-CH <sub>2</sub> CH <sub>2</sub> Ph	4.5 C <sub>1</sub> ≤ 10 C <sub>2</sub>	≤ 1	≤ 2
-CH <sub>2</sub> Ph	-	1.2	8.0
-CH <sub>2</sub> PhCH <sub>2</sub> CH <sub>3</sub>	5.3 C <sub>2</sub>	NR	NR

<sup>a</sup>Heating rate approximately 1000°C/s to a maximum temperature of about 800°C

<sup>b</sup>Unaccounted for and presumably added to the coal. Where the analysis of major fragment pieces was not reported ("NR"), this column was left blank.

TABLE 2  
ESTIMATED RATES OF HOMOLYSIS AND ANTICIPATED FRACTIONAL REACTION FOR GRAFTED LINKAGES

Coal Structure	Grafted Structure	BDE <sup>a</sup>	k <sub>homolysis</sub> (s <sup>-1</sup> ) <sup>b</sup>			Unconverted Fraction Remaining at T <sup>c</sup>			Unconverted Fraction Remaining at T <sup>d</sup> with 99% Recombination		
			650	700	750	650	700	750	650	700	800
Coal-O-	-nC <sub>3</sub> H <sub>7</sub>	61	8.4	4.9x10 <sup>-1</sup>	2.3x10 <sup>2</sup>	0.65	0.09	9.9x10 <sup>-6</sup> 1 x 10 <sup>-5</sup>	.996	.97	.89
Coal-O-	-CH <sub>2</sub> Ph	52	1.5x10 <sup>3</sup>	6.6x10 <sup>3</sup>	2.5x10 <sup>4</sup>	0	0	0	0.5	0.04	5 x 10 <sup>-6</sup>
Coal-O-	-CH <sub>2</sub> - 	47	2.3 x 10 <sup>4</sup>	8.7 x 10 <sup>4</sup>	2.9 x 10 <sup>5</sup>	0	0	0	1 x 10 <sup>-5</sup>	1 x 10 <sup>-19</sup>	0

<sup>a</sup>Estimated from values given in References 13 and 14. The assumption is made that coal structure bearing the oxygen atom is a single, unsubstituted phenyl ring. Inasmuch as this phenyl ring must have at least one other "substituent" to be a part of a polymeric coal matrix, this assumption provides an upper limit to the strength of the grafted linkage. Based on an E<sub>99</sub> = BDE + RT; A = 10<sup>13.5</sup> s<sup>-1</sup>.

<sup>b</sup>Unreacted Fraction = e<sup>-(k<sub>TS</sub>/A)(0.05)</sup>, where 0.05s is the time for the sample to heat from (T-50)°C to T<sub>final</sub> at 1000°C/s, the heating rate used by Zabransky and Stuck. Because k<sub>T-50</sub> is a lower limit to the rate constant during the last 50°C, the calculated value over-estimates the unreacted fraction.

<sup>c</sup>Unreacted fraction assuming 99% recombination is given by e<sup>-(k<sub>T-50</sub>)(0.05s)(0.01)</sup>, again an over-estimate of the unreacted fraction.

FROM ONE EXTREME TO THE OTHER: USING FUNDAMENTAL CHEMISTRY TO  
UNDERSTAND COAL BEHAVIOR OVER WIDE RANGES OF CONDITIONS

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Key Words: Kinetics, Polycyclic Aromatic Compounds, Model  
Compounds

Efforts to understand coal chemistry at a fundamental level face a good deal of complexity and uncertainty, but can also lead to major simplifications. Certain fundamental ideas have very broad applicability and can unify seemingly divergent aspects of coal behavior. Three such cases will be discussed. 1) With increasing coal rank and coal processing severity, increasingly strong bonds are broken. An overview of the "scissile" (weak) bonds present in coal and the conditions under which they cleave will be discussed, covering conditions from geothermal processing to fast coal pyrolysis. 2) While the chemical details of condensation reactions of polyhydroxy-benzenes are not entirely clear, these reactions cannot be avoided and it is probable that they determine the chemical properties of higher rank coals and underlie char-forming reactions in coal processing. A discussion of some of the implications of these reactions for coal chemistry will be presented. 3) Theoretical results suggest remarkably little dependence of the thermochemistry and free radical kinetics of polycyclic aromatic hydrocarbons (PAHs) on molecular size. This can lead to a considerable simplification in the analysis of coal char chemistry.

1) Simple Bond Breaking

Chemical bond dissociation follows a first-order rate law with the rate constant:

$$k_{\text{break}}/\text{s}^{-1} = 10^{15.0 \pm 1} \exp(-\text{Bond Dissociation Energy}/RT)$$

Given a characteristic time,  $t$ , for which the temperature  $T$ , has remained constant, bonds weaker than some bond strength  $\text{BDE}(T, t)$  will be unstable towards dissociation. For coal, characteristic times range from geologic ages ( $10^8$  years or  $10^{15}$  sec) to fast coal pyrolysis ( $10^{-3}$  sec) and temperatures from ambient to over 600 C. The types of bonds in coal with these characteristics will be pinpointed and discussed. They span the rather narrow range of bond strengths from 50 - 65 kcal/mol and include most varieties of alkyl-aryl ethers and 1,2-diarylethane linkages. The most significant scissile bonds in the thermal processing of coal are those just strong enough to have resisted dissociation under geothermal conditions.



## 2) Polyhydroxy aromatics

Studies of the reactions of dihydroxy-aromatic compounds by McMillen [1] and ourselves [2] demonstrate that at under conditions characteristic of coal liquefaction, these substances are almost entirely transformed into polymeric materials. Since the ortho hydroxy/alkoxy structure is the characteristic reactive unit in lignin and, presumably, in low rank coals and since these will ultimately form dihydroxybenzenes through dissociation pathways under coalification and coal processing conditions, these reactions are probably may be of central importance in the formation of high rank coals and char. A discussion of features of these reactions that are known and unknown will be presented.

## 3) Polycyclic Aromatic Hydrocarbons

These are characteristic products in the pyrolysis of virtually all hydrocarbons and are predominant in char and probably in anthracite coal. Theoretical studies [3] indicate that the edges of very large PAH clusters have chemical properties very similar to those of conventional and well-studied PAHs. Even at the edges of a layer of graphite properties of chemical structures depend very little on the long-range network of pi-electrons—instead individual sites behave in a manner similar to similar sites on convention PAHs. These "active sites" are the centers of reactions in both combustion and gasification.

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